

1917  
H87

Hultman

Improvements in the Preparation of  
P-Aminophenol and Some of its Derivatives



IMPROVEMENTS IN THE PREPARATION OF P-AMINOPHENOL  
AND SOME OF ITS DERIVATIVES

BY

IVAR NINUS HULTMAN

---

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

---

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1917



1917  
H87

UNIVERSITY OF ILLINOIS

..... May 31, ..... 1917..

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

..... Ivar Ninus Hultman.....

ENTITLED..... Improvements in the Preparation of p-Aminophenol.....

..... and Some of Its Derivatives.....

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF..... Bachelor of Science in Chemical Engineering.....

..... Oliver Kamm.....

Instructor in Charge

APPROVED:.....

W. A. Noyes

HEAD OF DEPARTMENT OF.....

Chemistry

376533

Feb. 17 C. Kelley



## T A B L E   O F   C O N T E N T S

PART I	<u>Preparation of p-Aminophenol</u>	pp
	Historical Part,	1
	Theoretical Part,	4
	Experimental Part,	
	(a) p-Nitrosophenol,	7
	(b) p-Aminophenol,	10
PART II	<u>Derivatives of p-Aminophenol</u>	
	Historical Part,	19
	Theoretical Part,	20
	Experimental Part,	
	(a) Dichloroanisidine,	22
	(b) p-Nitrosoanisol,	22
	(c) p-Nitrosophenetol,	23
	(d) Azophenol,	25
	<u>Summary,</u>	26
	<u>Acknowledgement,</u>	27

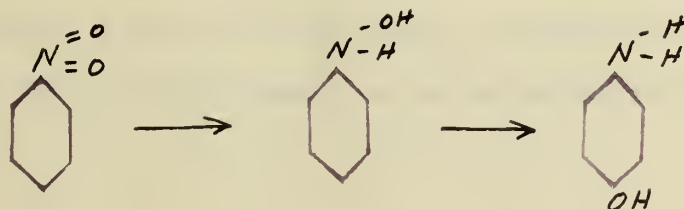




Improvements in the Preparation of  
p-Aminophenol  
and Some of its Derivatives

Historical

Numerous methods are given in the literature for the preparation of para-aminophenol. Baeyer and Caro<sup>1</sup> prepared it as a method of characterizing nitrosophenol by reducing the latter with tin and hydrochloric acid, allowing the hydrochloride to crystallize out of the reducing liquor. Griess<sup>2</sup> obtained it by the action of dilute sulfuric acid on diazobenzolimid. Friedländer<sup>3</sup> saponified phenolphthaloxim with dilute sulfuric acid, expecting to obtain beta-phenylhydroxylamine as one of the products, but found para-aminophenol instead. This rearrangement of beta-phenylhydroxylamine to para-aminophenol was later studied by Gatterman<sup>4</sup> who obtained aminophenol by the electrolytic reduction of nitrobenzene in concentrated sulfuric acid. Gatterman gives the following as the steps of the reaction:



- 
- 1 -- Ber. 7,863  
2 -- Ber.19,313  
3 -- Ber.26,177  
4 -- Ber.26,1844

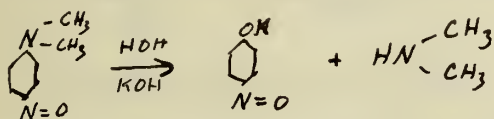


Digitized by the Internet Archive  
in 2013

One process<sup>5</sup> has been patented in which phenylhydroxylamine is rearranged to para-aminophenol by boiling with dilute sulfuric acid. Tauber<sup>6</sup> uses a method in which the 4-sulphonic acid of 4'-hydroxyazobenzene is fused with potassium hydroxide giving azophenol, which is then reduced to para-aminophenol by means of tin and hydrochloric acid.

Besides these that are specifically mentioned, there are numerous other methods by which the compound may be secured. For example, para-nitrophenol may be reduced by any of the common reducing agents, such as zinc dust, H<sub>2</sub>S in alkaline solution, and perhaps iron and hydrochloric acid; or nitrosophenol may be reduced by the same agents.

Paranitrosophenol was first prepared by Baeyer and Caro<sup>7</sup> who heated para-nitroso-dimethylaniline with dilute alkali, and obtained para-nitrosophenol and dimethylamine.



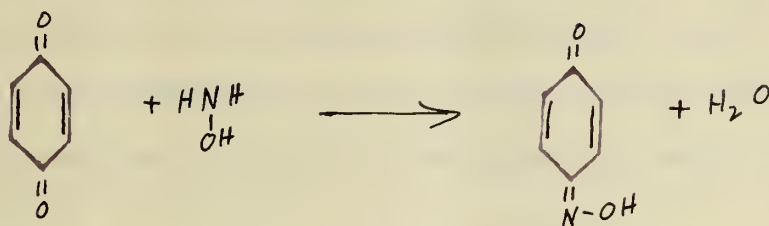
They studied its properties and other methods for its synthesis and report a method in which phenol is treated with a nitrite and acetic acid. Later<sup>8</sup> they succeeded in oxidizing para-nitrosophenol with nitric acid to para-nitrophenol, and also reduced the nitrosophenol to para-aminophenol.

-----  
 5 -- D.R.P. 83433, Friedl. 1899, p.53  
 6 -- D.R.P. 82426, Friedl. 1899, p.106  
 7 -- Ber. 7, p.809  
 8 -- Ber. 7, p.863

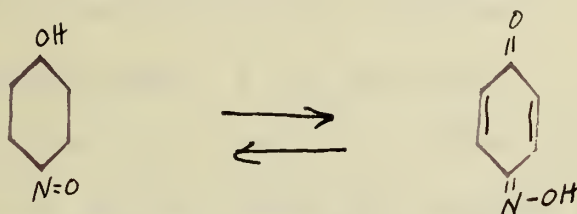




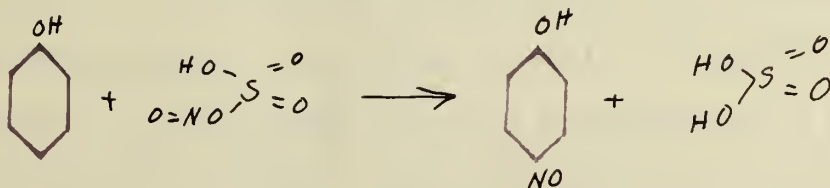
Goldschmidt<sup>9</sup> treated quinone with hydroxylamine hydrochloride and obtained benzoquinoneoxime.



This compound he found to be identical in all its properties with the para-nitrosophenol prepared by Baeyer and Caro, thus opening the way to a large field for investigational work. In a series of papers<sup>10</sup> he later proves, by working with the nitrosonaphthols, that if a nitroso and a hydroxyl group are on the same ring, in the 1-2 or 1-4 positions, the compound will be in an equilibrium between the true nitrosophenol and the quinoneoxime.



Stenhouse and Groves<sup>11</sup> prepared para-nitrosophenol in good yield by treating phenol with nitrosylsulfate. They report a yield of 96% of the theoretical in preparing the nitroso compound of resorcin by this method.




---

9 -- Ber. 17, 213  
 10 -- Ber. 17, 801, 2066, 18 568, 2224  
 11 -- Ann. 188, 360



Bridge<sup>12</sup> developed a method for obtaining paranitrosophenol by treating a dilute aqueous solution of sodium phenylate with sodium nitrite and adding dilute sulfuric acid. This method, with several modifications, was the one used for the preparation of para-nitrosophenol in the following experimental work.

### Theoretical Part

The principal disadvantage in using any of the common methods of reduction for obtaining para-aminophenol from nitrophenol or other substances lies in the fact that amino-phenol is very easily oxidized by the oxygen of the air, especially if the compound is in solution. An alkaline solution of amino-phenol in water is very rapidly colored a deep red due to the oxidation taking place in the solution. If the aminophenol is precipitated from such a solution after short exposure to the air, it will be colored brown and perhaps black. It is well known that polyhydroxyphenols and polyaminobenzenes are very easily oxidized, and the fact that aminophenol contains both an amine and a phenolic group no doubt accounts for this ease of oxidation.

In order to develop an ideal method for the preparation of para-aminophenol it is first of all essential that the parent substance be a compound that may be obtained in good yields, and in order to assure a good yield and at the same time a high grade of purity, it is desirable that the parent substance be made by a process that will give a para compound only,

-----





and not a mixture of two compounds that would have to be separated from each other before the reduction to para-aminophenol. If para-nitrophenol is to be used as a starting point, it must be first purified from the ortho compound and this will cause a decrease in yield on the phenol as a basis. A reducing atmosphere should be present during the entire progress of the reaction to protect the aminophenol from oxidation of the air, and the aminophenol should be easily recoverable from the reaction liquor. The latter requirement is an objection to the methods ordinarily used.

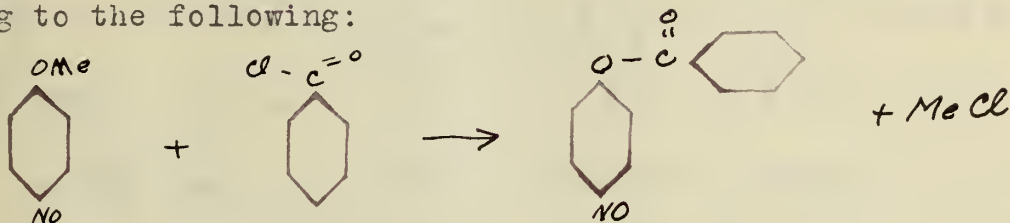
To fulfill the first condition, the compound that will most nearly fill all the requirements is para-nitrosophenol, and this product was used as a starting-point throughout the experiments.

The yield, ease and cheapness of preparation, and original purity of nitrosophenol are points that are very much in favor of its being used as starting point in the preparation of para-aminophenol, if a suitable method for its reduction to para-aminophenol can be developed. It may be obtained in very good yields from phenol by the action of nitrous acid, and is formed without being contaminated with ortho-nitrosophenol or other compounds from which it would have to be separated before being converted into para-aminophenol.

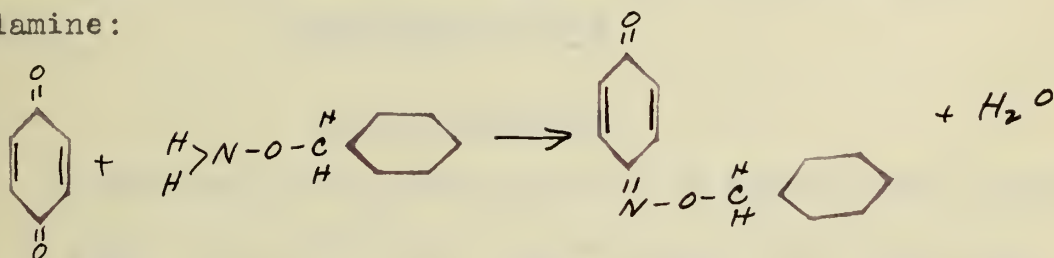
Much work has been done on the shifting of structure of para-nitrosophenol to quinoneoxime. In many cases the compound reacts as if it were entirely in the quinoneoxime form.



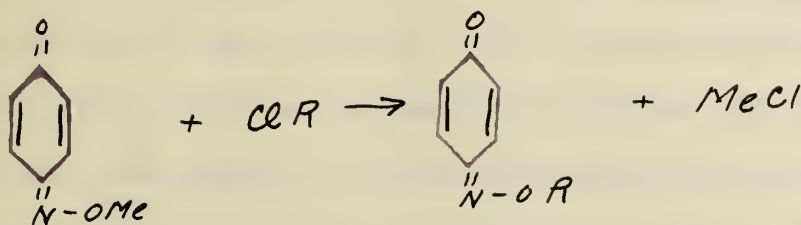
For instance, Walker<sup>13</sup> prepared what he thought was the benzoyl ester of nitrosophenol by adding benzoyl chloride to the sodium salt of nitrosophenol, expecting that the reaction would go according to the following:



Bridge<sup>14</sup> by an analogous method, later prepared the benzyl ether of nitrosophenol by treating the sodium salt of the latter with benzyl chloride. He also prepared the same compound by an entirely different method, treating quinone with alpha-benzylhydroxylamine:



The two compounds were identical in color, melting point, etc., proving that the salts of para-nitrosophenol are formed from the oxime structure, and not from the phenol form, and that ethers of nitrosophenol are formed according to the following general reaction when the ordinary methods of preparing ethers are used:

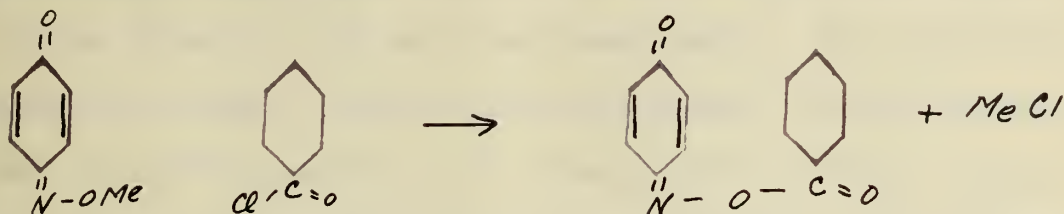


13 -- Ber. 17, 399  
14 -- Ann. 277, 79





For example, the benzoyl ester prepared by Walker was formed by the following reaction.



Bridge makes the statement that the compound is entirely in the oxime form, but the work done by others, and the following experiments suggest that the structure is an equilibrium between the two forms, the equilibrium changing according to the reagents with which the compound is treated.

### Experimental Part

#### p-Nitrosophenol.

Bridge prepared p-nitrosophenol by dissolving 60 grams phenol, 54 grams sodium nitrite, and 27 grams sodium hydroxide in 1500 cc water, cooling to 7 deg. and adding slowly and with continual stirring a cold mixture of 150 cc concentrated  $\text{H}_2\text{SO}_4$  in 400 cc water. The nitrosophenol precipitates, is filtered off, washed with ice water, and purified from ether.

This method was used, with several modifications, in making the nitrosophenol required in the following work. Bridge used an excess of 25% nitrite, but it was found by experiment that the yield could be increased by increasing the nitrite to 35% excess. The phenol, sodium hydroxide, and nitrite were dissolved in 1500 cc water, cooled to 5-7 deg. and the acid added slowly with continual stirring. The rate of adding the



acid was adjusted so that ten minutes were required for all of the acid to be added. The solution remained clear for three or four minutes after all the acid had been added. The nitrosophenol precipitated in small, light brick red flakes, The stirring was continued for thirty minutes, the precipitated nitroso compound allowed to settle, and the solution then filtered. The nitroso-phenol was washed with ice water and dried. The average yield was 70% of the theoretical, and the product was pure enough to be used directly without further purification.

In several runs, in which the amount of water used was slightly less than 1500 cc, a black tarry substance separated out and floated on the surface of the liquid when the solution was acidified. On investigation the substance proved to be composed largely of phenol. It is evident that the volume of the solution was too small to dissolve all the phenol in the presence of another acid. To counteract this effect the dilution was increased to 1800 cc. From this volume<sup>m</sup> of solution the nitroso-phenol obtained had a lighter color, and the yield was decreased only slightly.

Two trials were run in parallel using tenth portions of a regular run in one trial, and omitting the alkali and a corresponding amount of acid in the other, to determine whether or not the alkali was necessary. If the solution without alkali is sufficiently dilute and kept well agitated, the phenol will stay in solution. The yield in the trial without alkali was 60%, a reduction of 10%. It is peculiar that the yield should be decreased when alkali is not used, since the alkali must first be





neutralized before any nitrous acid is generated. The larger dilution cannot account for the large decrease. Trials in which the alkali was reduced to one-half, with a corresponding decrease in the acid gave results that were practically as good as when the full quantity of alkali was use, but the dilution must be slightly greater to keep the phenol in solution. This method also gave a mother liquor that was very satisfactory to use over again.

Nitrosophenol is soluble in cold water to the extent of approximately one part per hundred, and even with the acid and sodium sulfate present, which have a salting-out effect, it is evident that a considerable quantity of it must be in solution in the two liters of mother liquor that are left after the product has been filtered. To recover this product, the mother liquor may be used for making another portion of nitrosophenol. The disadvantage of this process lies in the fact that sodium sulfate is only slightly soluble in cold water, and may crystallize out of the solution when the strongly acid mother liquor is neutralized with strong alkali and used again without further dilution, thereby contaminating the product. For this reason it is necessary to reduce to a minimum the amount of alkali and acid used. The following quantities gave results that were very satisfactory: 30 g phenol, 30 g  $\text{NaNO}_2$ , and 6.7 g  $\text{NaOH}$  were dissolved in 800-900 cc water, cooled to 5-7 deg. and a cooled solution of 65 cc concentrated  $\text{H}_2\text{SO}_4$  in 200 cc water added slowly with continual and vigorous stirring. The nitrosophenol was allowed to remain in the solution for an hour, and



was then filtered and washed with ice water. The mother liquor was neutralized with sodium hydroxide, diluted to 1200-1300 cc and another similar run made.

The product of the second portion may vary widely in quality, sometimes being as good if not better than the first product, and at other times being of a pale brown color, without the typical red shade, and turning almost black on exposure to the air for any length of time. A uniform product with good keeping qualities may, however, be obtained by carefully regulating the experimental conditions. The yield is increased to 80% on the average, sometimes being as high as 83%.

#### p-Aminophenol

Reduction of para-nitrosophenol to para-aminophenol by reduction with iron, as in the commercial production of aniline.

12 g nitrosophenol were added in small portions to a mixture of 40 g iron powder, 50 cc water, and 4 cc concentrated HCl. Much heat was generated in the first stages of the reaction and the flask had to be cooled frequently while the first portions of the nitrosophenol were being added. Later the reaction became slower and the flask was warmed at intervals. When all the nitrosophenol had been added, the flask was placed on the water bath for ten minutes, with frequent shaking. The iron was then filtered off hot and the solution cooled. The liquid was colored almost black and soon became covered with a layer of dark brown substance. Nothing separated out on cooling, so the solution





was allowed to stand. After two days a small quantity of black substance had crystallized out. This was filtered off and proved to be the hydrochloride of aminophenol. It was attempted to obtain the free base by neutralizing the acid solution with  $\text{NaHCO}_3$  and extracting with ether, but this was unsatisfactory because of the low solubility of aminophenol in ether.

In one experiment the iron was allowed to react with the acid and nitrosophenol then added to the mixture and reduced. When all the nitrosophenol had been added the solution was extracted with ether, giving a fairly good yield of aminophenol of a light purple color, melting with decomposition at 184-186 deg.

Neutralizing the acid and precipitating the iron in solution as the hydroxide, filtering, and acidifying with a weak acid is unsatisfactory because of the difficulty of filtering the hydroxide and the rapid oxidation of aminophenol in alkaline solution.

From the experiments made, it seems certain that the iron reduction method is not suitable for the preparation of p-aminophenol from p-nitrosophenol, chiefly because of the ease with which the aminophenol oxidizes in solution. This oxidation is materially increased by the ferric salts formed during the reduction.



### Reduction with Hydrogen Sulfide

Reduction of nitrosophenol in alcoholic solution by means of hydrogen sulfide, whether with or without the addition of acids or alkalies, appeared to be the most feasible method for the production of aminophenol. The  $H_2S$  will maintain a reducing atmosphere during the entire process, protecting the aminophenol from oxidation by the air after it has been formed.

All the methods given in the literature for reducing with  $H_2S$  recommend using a solution of the compound in alcohol, adding an alkali or other agent to assist in the reduction and passing the  $H_2S$  into the refluxing solution. For reducing nitrosophenol to aminophenol with  $H_2S$  this method was useless. In fact, it was found that the colder the solution could be kept, the better would be the color and yield of the product, and that agitation was just as important as keeping the solution cold.

Gatterman<sup>15</sup> gives a method for reducing dinitrobenzene to meta-nitraniline by means of  $H_2S$  and  $NH_4OH$ . This method was applied to reducing p-nitrosophenol to p-aminophenol by passing  $H_2S$  into the refluxing solution of 15 g nitrosophenol in 250 cc ethyl alcohol and 10 cc conc. ammonia water, and determining the gain in weight. The solution turned very dark brown, almost black, soon after it was heated to boiling, and remained that color. No sulfur appeared. After refluxing for four hours, the gain in weight was 5.5 g. The theoretical gain for 15 g nitrosophenol reduced to aminophenol is 4.8 g. The solution became viscous on cooling and a small quantity of a black





substance precipitated. When small portions of the viscous liquid were poured into water, nothing separated out. It was evident from this trial that a reduction in a refluxing solution could not be used or adapted for use in this case, and no further work was done on the method.

Reduction with  $H_2S$  under Varying Conditions.

Three portions of nitrosophenol of approximately 0.5 g each were dissolved in 25 cc portions of alcohol, a few drops of HCl added to one portion, a little KOH solution to another, and the third reduced with neither acid nor alkali. The solutions were warmed to about 45 deg. on the water bath and  $H_2S$  then passed into the three portions for several minutes without any vigorous agitation. No sulfur appeared and there was no heat developed but when the test tubes were shaken, the solutions warmed up rapidly and sulfur was precipitated in all portions. On standing exposed to the air for a few minutes the solution containing alkali turned distinctly brown, the one containing HCl slightly so, while the one without acid or alkali remained a clear straw yellow color. This shows that the use of either acid or alkali in the reduction should be avoided if possible, since it tends to hasten the oxidation of the aminophenol, and in this case is not essential to the reduction. The sulfur was filtered off from the hot solutions, and the solutions allowed to cool and stand for several hours. A small quantity of crystals appeared in all the samples. The solutions were cooled to 0 deg. and more crystals separated. These were filtered off and dried on a clay plate. Their color was a dark



brown, lighter in the case where no acid or alkali was used, The crystals melted with decomposition at 185-188 deg.

Other portions were tried in which the concentration of the nitrosophenol was varied. If the solution was very concentrated, the sulfur seemed to be precipitated with difficulty and the aminophenol was consistently of a dark brown color. Agitation was essential to the separation of the sulfur. In one portion  $H_2S$  was passed into the solution for three or four minutes without the appearance of ~~form~~ sulfur, but as soon as the flask was shaken the sulfur precipitated with an appreciable evolution of heat. All the above portions were warmed to 40-50 deg. on the water bath before the reduction was begun, and when the sulfur was precipitated the temperature rose rapidly to close to 70 deg. Undoubtedly the dark color of the aminophenol was due to partial decomposition at the high temperature at which the reaction took place. The results were far different when the solutions were cooled to 0 deg. or below before  $H_2S$  was passed in.

Reduction with  $H_2S$  in the cold.

One gram nitrosophenol was added to 25 cc alcohol, the solution cooled to 0 deg. and  $H_2S$  passed in with continual shaking. In one minute the solution warmed to 20 deg and the sulfur precipitated. The sulfur was filtered immediately and more  $H_2S$  passed in to determine whether or not the reduction was complete. No more sulfur appeared in three minutes, and the temperature did not rise further. The solution was cooled to -10 deg. and a few light yellow crystals of aminophenol





appeared. These were not filtered off. Another gram of nitrosophenol was added to the same solution and the latter again saturated with  $H_2S$  at 0 deg. or below. The sulfur was filtered off while the solution was still warm from the heat of the reaction. On cooling to -10 deg this time a large quantity of aminophenol crystallized out and was filtered off and washed with ice water. The crystals when filtered and washed had a metallic luster, resembling finely divided aluminium. On exposure to the air the color turned to a faint blue and then ~~to a~~ to a dirty gray. By keeping the solution very cold while reducing, a product could easily be obtained which was absolutely white or cream colored, and by thorough washing, this color could be preserved for a long time even on exposure to the air.

To determine the efficiency of this method of preparing aminophenol from phenol, 30 g phenol were converted to nitrosophenol, giving a yield of 28 g., equivalent to 71% of the theoretical. The nitrosophenol was divided into seven equal parts of 4 g each and reduced with  $H_2S$  in the cold by the following method.

100 cc ethyl alcohol was cooled to 0 deg., saturated with  $H_2S$  in a 250 cc wide mouthed flask, and one 4 g portion of nitrosophenol dissolved in it. A rapid stream of  $H_2S$  was passed into the flask for a few seconds to remove most of the air, the flask stoppered with a rubber stopper containing a glass tube through which the  $H_2S$  was passed in, and placed in a vibrating agitator operated by an electric motor. The  $H_2S$  was passed in under a pressure of 6-7 inches of water from a



Kipp generator, and was free to enter as it was absorbed by the solution. The sulfur appeared in about three minutes, with a rise of temperature of about 25 deg. The agitation was continued for a few minutes longer to insure complete reduction. The original solution of nitrosophenol was a dark brown color, but after the reduction was complete it had changed to a light yellow. The flask was removed from the agitator, the sulfur filtered off, and the alcohol solution cooled to -10 deg by a freezing mixture. A large quantity of aminophenol crystallized out in small glittering leaflets, which when filtered and washed with ice water were a light cream color, turning a blueish gray on exposure to the air.

Another portion of nitrosophenol was added to the filtered mother liquor and the flask replaced in the agitator before the solution had warmed to above 0 deg. and the process repeated with the other portions. The second and succeeding portions solidified to a mass of crystals on cooling to -10 deg. The mother liquor contained a few grams in solution throughout the reductions since aminophenol is soluble in alcohol to the extent of 4.5 parts in a hundred at 0 deg. The mother liquor was evaporated and the dissolved aminophenol recovered and included in the total yield. The color of the recovered aminophenol was quite dark due to decomposition on evaporating the alcohol. The total yield of aminophenol from 30 g phenol was 13.5 g, a yield of 54.4% from nitrosophenol and 38.5% from phenol.





Several points must be observed in using this method of reduction. The solution of nitrosophenol in alcohol must not be too concentrated, or some aminophenol will crystallize out of the warm solution and be filtered off with the sulfur. To prevent this loss the filtered sulfur was washed with a few cc warm alcohol. This of course dilutes the mother liquor slightly, but also makes up for the loss of alcohol remaining in the sulfur<sup>5</sup> and aminophenol when they are filtered off.

The flask must be swept free from air by means of the  $H_2S$  before the stopper is inserted, or the absorption of the  $H_2S$  will be very slow. Several times, when the stopper was placed before the gas was turned on, the reduction would not take place at all. When the stopper was removed and a lively stream of  $H_2S$  passed through the solution the sulfur precipitated almost immediately. The reduction works much faster when a continual stream of  $H_2S$  is passed through the solution but because of the nuisance caused by the escaping gas, the following method was used. The flask was swept free from air by  $H_2S$ , the stopper inserted, and the agitation begun. The gas was then free to enter as it was absorbed by the solution, being also under pressure from the Kipp generator. It is advisable to keep the hands from coming in contact with the solution of nitrosophenol or aminophenol since it leaves a brown stain which is very difficult to remove.

A few cc acetic anhydride were added to a small amount of aminophenol in a test tube. Heat was generated. The solution was very light purple. After boiling the solution for



three minutes it was allowed to stand for twenty-four hours. Crystals of the acetyl derivative had separated out, which when filtered and washed with water were perfectly white. The compound was purified by dissolving in hot water and cooling. The melting point of the derivative was 150 deg.

Reduction of Nitrophenol by  $H_2S$  alone.

5 g paranitrophenol were dissolved in alcohol and  $H_2S$  passed in with agitation. There was no change in color, and no sulfur precipitated either in the cold or after being heated.





P A R T    II

Derivatives of p-Nitrosophenol

Historical Part

Ter Meer<sup>16</sup> prepared many salts of p-nitrosophenol, assigning to them the true nitrosophenol structure:



but from the work done by Bridge<sup>17</sup> it is evident that he obtained the salts of the quinoneoxime form, and that the true structure was



Ter Meer also attempted to prepare ethers of nitrosophenol, but without success. He mentions the remarkable action of a solution of hydrochloric acid gas in alcohol on nitrosophenol.

Jaeger<sup>18</sup> studied the action of various solutions of hydrochloric acid gas on nitrosophenol and obtained the following results. When nitrosophenol was boiled with dilute aqueous hydrochloric acid, the nitroso group was replaced by a chlorine atom with the formation of chlorophenol, which could be recognized by its odor. When the nitrosophenol was added to a cold concentrated solution of hydrochloric acid gas in

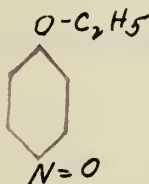
-----  
16 -- Ber 8, 623  
17 -- Ann. 277, 79  
18 -- Ber. 8, 894





ether, a dichloroaminophenol was formed. In a solution of hydrochloric acid gas in ethyl alcohol, a dichlorophenetidine was obtained.

Baeyer and Knorr<sup>19</sup> treated p-phenetidine with Caro's acid and succeeded in oxidizing the amine group to a nitroso group, thus preparing for the first time one of the normal ethers of p-nitrosophenol possessing the structure



The compound was later proved to be a mixture of nitrosophenetol and nitrophenetol, which resulted in a high melting point.

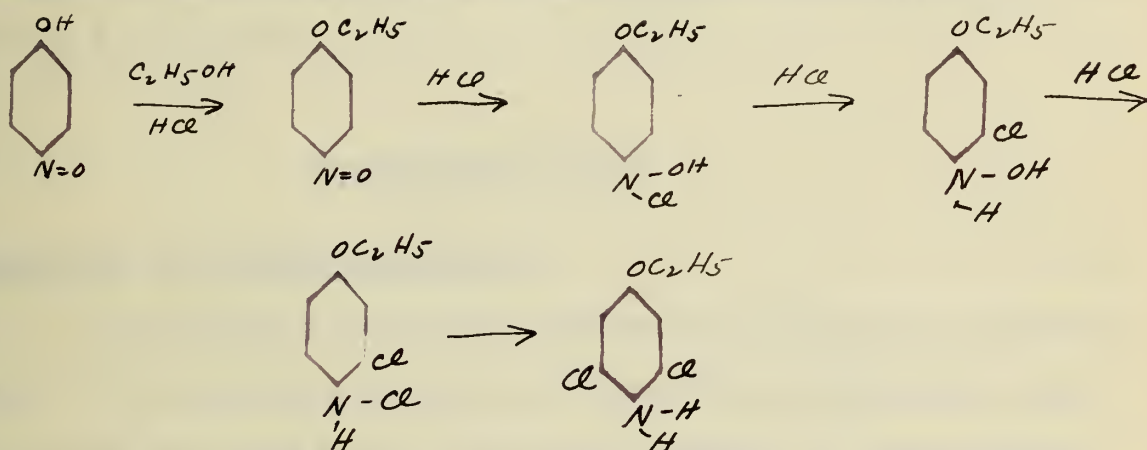
Rising<sup>20</sup> prepared the ethers of p-nitrosophenol by the following method. p-Nitrophenetol was treated with zinc, giving beta-phenetolhydroxylamine. This compound was dissolved in alcohol and dropped into a solution of ferric chloride. The light green solid formed was filtered from the solution and dried. Its melting point was 33-34°. The corresponding methyl ether prepared in an analogous manner from p-nitroanisole was also light green and melted at 23°.

#### Theoretical Part.

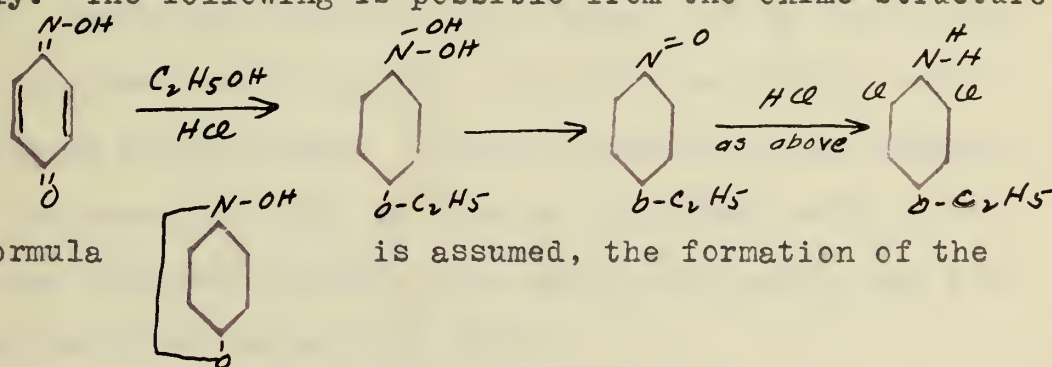
The ease with which a cold solution of hydrogen chloride in ethyl alcohol will react with nitrosophenol and the



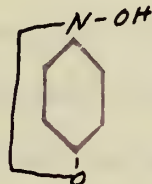
great changes which are produced on the compound are very remarkable. The nitroso group is reduced, new groups are introduced into the ring, and the phenolic hydroxyl group is converted into an ether. These changes make it seem very probable that the tautomeric nature of nitrosophenol plays an important part in the reaction. The mechanism of the changes may be explained in several ways. If the nitrosophenol is assumed to have the true nitrosophenol structure, the following looks plausible:



The positions of the chlorine atoms have not been determined definitely. The following is possible from the oxime structure:

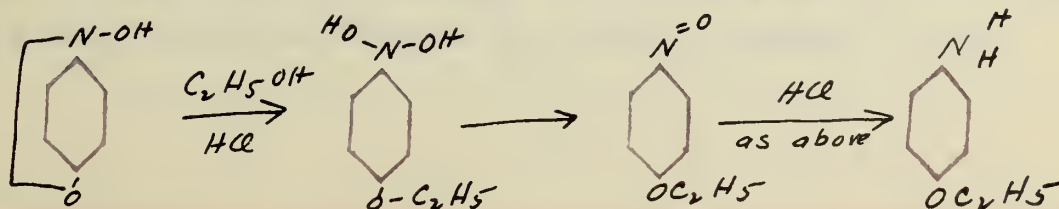


If the formula



is assumed, the formation of the

ether could be explained by saying that the bond between the oxygen and the nitrogen is broken, and alcohol added, as follows:







In any case, it should be possible to stop the reaction at the ether formation, before the nitroso group has been affected by the hydrochloric acid present. All previous attempts, however, to prepare these normal ether of nitrosophenol have resulted in failure. In the following experimental part it is shown that the normal nitroso ether is actually the first step in the action of alcoholic hydrochloric acid gas upon p-nitrosophenol. The normal ethers of p-nitrosophenol have been isolated and their identity established.

### Experimental Part

#### Preparation of Dichloroanisidine.

Two grams of freshly prepared nitrosophenol were dissolved in 25 cc methyl alcohol which had been previously saturated at 0° with HCl gas. The mixture warmed up considerably after two minutes shaking and then solidified to a mass of crystals. These were filtered off, washed with a little alcohol and dissolved in dilute HCl. On addition of NaOH solution the free base precipitated. This was distilled with steam and dried. The base distilled as a white flocculent white solid. Its melting point was 72-73°. Its acetyl derivative was prepared and was found to melt at 189°.

#### p-Nitrosoanisol.

Two grams nitrosophenol were dissolved in cold methyl alcohol saturated with HCl gas, the solution shaken for one



minute and then poured into 150 cc water before any rise in temperature was noticeable. A light blueish green color appeared first, changing soon to a very dark green. When made alkaline the solution became dark red. On distillation with steam a light green solution distilled over first. When this solution was extracted with ether and the ether evaporated off, a blueish green, low melting solid with a rich odor remained. Its melting point was found to be 22 deg., which agrees well with the value reported by Rising. The methyl ether of quinoneoxime is a yellow solid, as reported by Bridge.

p-Nitrosophenetol.

Two grams of nitrosophenol were dissolved in 30 cc ethyl alcohol saturated with HCl gas. The solution was allowed to stand for one minute and was then poured into 150 cc cold water. The same color changes appeared as in the experiment with methyl alcohol. On extracting the light green solution which was obtained by steam distillation of the neutral solution, with ether and evaporating the ether, a green solid remained. Its color and odor were very similar to the color and odor of p-nitrosoanisol. The color became a light blueish green on recrystallization from ether. Its melting point was 32-33°.

A portion of the nitrosophenetol was dissolved in alcohol and H<sub>2</sub>S passed through the solution. The color changed to yellow in a few seconds, but only very little sulfur appeared. A solid consisting partly of sulfur remained after evaporating the alcohol. Intermediate reduction products were formed.

Another portion of nitrosophenetol was reduced by





iron. Dilute HCl was allowed to act on iron until the acid had been completely converted into ferrous chloride. Small portions of the ether were then added slowly and with stirring. The color and odor of the nitrosoether soon disappeared. The iron mixture was extracted with ether and the ether evaporated leaving a brown liquid. This was extracted with dilute HCl to remove phenetidine, the HCl made alkaline with NaOH, extracted with ether and the ether evaporated. A light brown liquid was left, which upon distillation under ordinary pressure yielded a colorless liquid boiling at  $247^{\circ}$ . This value agrees with the boiling point of p-phenetidine. The residue from the ether extraction of the iron after removing the phenetidine was purified. It melted to a translucent liquid at  $136-137^{\circ}$ , and cleared up at  $167-169^{\circ}$ . The temperature range between  $136^{\circ}$  and  $167^{\circ}$  is accounted for by the formation of liquid crystals as reported by Gatterman.

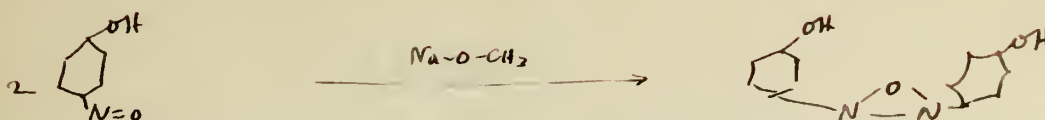
#### Other Derivatives of p-Nitrosophenol.

Other methods of preparing derivatives of p-nitrosophenol were attempted, such as boiling a solution of NaOH and nitrosophenol in alcohol, and also a solution of nitrosophenol alone in alcohol, but in every case, the prolonged heating had a decomposing effect on the nitrosophenol and the results were negative.

It was hoped that the well-known method of preparing azoxybenzene from nitrobenzene by the action of sodium alcoholate could be applied to nitrosophenol for the production of azoxyphenol.







The above reaction, however, did not take place.

### Azophenol.

Schraube<sup>21</sup> treated p-nitrosodimethylaniline with aniline acetate and obtained 4-dimethylaminoazobenzene.

Kimich<sup>22</sup> prepared 4-hydroxyazobenzene by a similar method from nitrosophenol and aniline acetate. By analogy, to these syntheses, azophenol should be obtained by treating aminophenol acetate with nitrosophenol. This was attempted by Weselsky and Benedikt<sup>23</sup> without success.

Two grams of nitrosophenol, 1 gram aminophenol dissolved in acetic acid were allowed to stand for 24 hours. At the end of that time a small quantity of a black substance had precipitated from the dark brown liquid. Nothing further was done with the solution.

---

21 -- Ber. 8, 616  
22 -- Ber 8, 1026  
23 -- Ann. 196, 343



## S U M M A R Y

The method of making p-nitrosophenol by the action of nitrous acid on phenol has been improved by using the mother liquor for a second run, thereby recovering the product dissolved.

A new method for the production of p-aminophenol has been developed. P-Nitrosophenol is reduced in alcohol solution by means of hydrogen sulfide without the addition of acid or alkali. The aminophenol is recovered by allowing it to crystallize from the cooled solution in alcohol, and the mother liquor is used repeatedly. The p-aminophenol obtained possesses a high grade of quality.

The action of hydrochloric acid gas dissolved in alcohol, on p-nitrosophenol has been studied, and intermediate products of the reaction obtained. It has been shown that the first step in the reaction is the formation of the normal ethers of p-nitrosophenol.

The normal ethers of p-nitrosophenol have for the first time been obtained directly from the corresponding nitroso compound. All previous attempts had resulted in the formation of ethers of quinoneoxime.



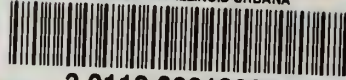


IN CONCLUSION, I wish to express to Dr. Oliver Kamm, under whom this work was undertaken, my deep appreciation for his many and valuable suggestions during the progress of the experiments.





UNIVERSITY OF ILLINOIS-URBANA



3 0112 082199206